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**TITLE:** Materials Research Society Symposium Proceedings; Volume 720. Materials Issues for Tunable RF and Microwave Devices III Held in San Francisco, California on April 2-3, 2002

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## Synthesis of Nanostructured Magnetic Mixed-Oxide Ferrite Powders by Using A Novel Chemical Method

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### ABSTRACT

In the present investigation, an attempt has been made to establish a new chemical route for synthesis of the nanostructured mixed oxide ferrite powders. By using this chemical method a variety of ferrite powders having spinel structure and doped with Co, Ni, Mn, Zn etc has been prepared. In this method nitrate salts of the different metals were used as starting materials. The aqueous solutions of the metal nitrates were mixed according to the molar ration of the compositions. Then the mixtures were mixed with an aqueous solution of water soluble polymer (polyvinyl alcohol). This mixture after drying yield fluffy brown powders. These powders were then calcined at different temperatures ranging from 400 °C to 700 °C. Nanostructured powders were obtained from the thermal decomposition of the brown powders. The powders, prepared by calcinations at different temperatures, were characterized by using X-Ray diffraction analysis, IR spectroscopy, TGA/ DTA, and TEM. It was observed that the average particle size of the powders are in nanometer scale with a narrow size distribution. The average particle size of the powders was increased with the increase of calcinations temperature.

This chemical method has proved to provide a convenient process for the preparation of nanostructured ceramic powders at comparatively low temperatures and offers the potential of being a simple and cost-effective route.

### INTRODUCTION

Research in the field of nanostructured ceramic powders have gained immense importance because of their potential application in many areas of technology. Technologically, fine-particle ferrites have been of interest due to their wide spectrum of applications as inductor cores in RF systems, circulators, permanent magnets, advanced memories, sintered electrodes, microwave devices, anti-detection (stealth) technology applications, catalysts etc. The surface properties and the microstructures of such powders, which control most of the parameters required for any particular application, often depend on the method of their preparation. Conventional solid state reactions described as ceramic techniques do not provide nanostructured ferrite materials having homogeneous composition. In the conventional ceramic method for the preparation of ferrites long heating schedules and high temperatures, sinter the final product and result in the loss of the fine particle nature of the powders. This method is thus affected by a poor control of the particle size, morphology and microscopic homogeneity (1).

The chemical synthesis routes for the production of fine ferrite powders have overcome many of the limitations of the ceramic method. The important chemical synthesis routes, which have gained substantial popularity over the years, include the precursor compound method, the co precipitation method, the sol-gel method, the solvent evaporation method, the hydrothermal method and the combustion method (2-12).

Although several chemical routes exist for the preparation of fine ferrite powders, the consideration of affordability and versatility of a route still remain a major challenge for the materials scientists, involved in the development of new synthetic routes. In the present investigation, a novel chemical route which is both affordable and versatile for the synthesis of a series of ferrite powders has been developed. By using this chemical method ferrites having general formula  $MFe_2O_4$  [where  $M = Ni(II), Co(II), Zn(II)$ ] has been prepared.

## EXPERIMENTAL METHOD

### Preparation of the precursor materials for $MFe_2O_4$

To prepare precursors of the mentioned oxide systems appropriate amounts of the desired metal nitrates were taken into aqueous solution. 10%(w/v) aqueous solution of a water-soluble polymer (Polyvinyl alcohol) is then added to each of the mixed metal nitrate solutions.

An aqueous solution containing equal weight percentage of sucrose and tartaric acid (20 wt%) was prepared. 50ml of this mixture was added to the of water soluble polymer and metal nitrates. This resulting viscous liquid mixture was evaporated to dryness to obtain a voluminous organic based fluffy precursor powder.

Ultrafine ferrite powders were obtained by calcining the precursor powders at varying temperature ( $400^{\circ}C$  to  $700^{\circ}C$ ) for varying periods of time.

Thermal gravimetric and differential calorimetric (TG/DSC) studies of the precursor material, were performed on the STA-625 thermal DSC. All experiments were performed in air atmosphere with a heating rate of  $10^{\circ}C/min$ . the infrared spectra for the precursor and the heat treated powders were recorded on the Perkin Elmer 883 infrared spectrophotometer from 400 to  $4000\text{ cm}^{-1}$  by the KBr pellet method. The X-ray powder diffraction (XRD) patterns for the precursor and the heat treated powders were recorded using Phillips P.W. 1710 X-ray diffractometer with  $CuK_{\alpha}$  radiation and Nickel filter. Transmission electron microscopy (TEM) studies of the prepared powders were done on CM-12 Phillips electron microscope. A vibrating sample magnetometer was used for the room temperature magnetic studies of the prepared powders.

## RESULTS AND DISCUSSION

The simultaneously recorded TG and DSC data for the  $NiFe_2O_4$ ,  $CoFe_2O_4$  and  $ZnFe_2O_4$  precursor powders produced, by this chemical method, follow a similar trend. The thermograms reveal that the precursor powders involve a single step decomposition between  $200^{\circ}C$  to  $400^{\circ}C$ . The precursor powders are found to decompose between  $210^{\circ}C$  to  $360^{\circ}C$  with an exothermic peak at  $302^{\circ}C$ . The process involves an exothermic heat liberation of 300 kcal/mg with 35% weight loss. The exothermic heat liberation is due to the combustion of the carbonaceous remains of the polymer and decarboxylation of the precursor material, which is accompanied by the evolution of gases such as  $CO$ ,  $CO_2$  and  $H_2O$  (water vapor). The thermal effects are thus accompanied by weight loss in TG curve.

The XRD of the ferrite powders, produced by this chemical route, reveals that the precursor powders are X-ray amorphous. From XRD spectra it was found the  $\text{NiFe}_2\text{O}_4$  first formed when its precursor powder was calcined at  $400^\circ\text{C}$  for 5hrs. A broad XRD peak corresponding this ferrite phase was observed. Similarly  $\text{CoFe}_2\text{O}_4$  and  $\text{ZnFe}_2\text{O}_4$  were formed when their precursor powders were calcined at  $500^\circ\text{C}$  for 4 hrs and  $550^\circ\text{C}$  for 6hrs. The XRD peaks, corresponding to the ferrite phase, increase in intensity with subsequent heat treatments. This indicates the growth of crystallinity in the powders with increase in heat treatment temperature and time.

IR spectra of all the precursor powders and powders prepared by calcinations of precursors was taken. In the precursor powders IR bands at  $3387\text{ cm}^{-1}$  and  $1619\text{ cm}^{-1}$  are due to the presence of moisture in the materials. The intensity of these bands diminishes and vanishes with the increase in heat treatment. The absorption bands at  $1394\text{ cm}^{-1}$ ,  $1087\text{ cm}^{-1}$ , and  $822\text{ cm}^{-1}$  in the precursor materials, can be assigned to the various vibrational modes of carboxylate ions. These absorption bands disappear after heat treatment at  $450^\circ\text{C}$ . The absorption bands at  $578\text{ cm}^{-1}$  and  $420\text{ cm}^{-1}$  were observed for calcined powders are due to the lattice absorption of metal ferrites. These band intensity increases with increase in heat treatment temperature.

The crystallite size of the prepared powders are determined from XRD line broadening using the Scherrers' equation. These studies reveal that with the increase in the calcinations temperature the crystallite size gradually increases for all the powders. The average particle size of the powders prepared by calcining at different temperature with varying calcinations time was measured by TEM. The average particle size of the powders of  $\text{NiFe}_2\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4$  and  $\text{ZnFe}_2\text{O}_4$  are shown in table1. From TEM it was observed that the average particle size of the powders are in nanometer scale ( $\pm 10\text{ nm}$ ) with a narrow size distribution.

Table 1 Average particle size (nm) of the powders calcined as different temperatures.

Sample	Calcination Temperature								
	$500^\circ\text{C}$			$600^\circ\text{C}$			$700^\circ\text{C}$		
	4 hrs	6 hrs	10hrs	4 hrs	6 hrs	10 hrs	4 hrs	6 hrs	10 hrs
$\text{NiFe}_2\text{O}_4$	40nm	45nm	54nm	53nm	65nm	74nm	65nm	78nm	80nm
$\text{CoFe}_2\text{O}_4$	35nm	42nm	49nm	57nm	68nm	74nm	63nm	74nm	82nm
$\text{ZnFe}_2\text{O}_4$	37nm	45nm	56nm	61nm	70nm	75nm	70nm	80nm	85nm

## CONCLUSION

A number of nanosized ferrite has been prepared by using a novel chemical method. This method is technically simpler, cost effective, and more time and energy- efficient than the other reported methods for preparation of single phase mixed-oxide powders. This chemical route has the potential to apply for synthesis of a variety of mixed oxide systems at relatively low temperature.

## ACKNOWLEDGEMENT

The author is thankful to Third World Academy of Sciences for granting financial support of this research project.

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